Samarium *versus* aluminium Lewis acidity in a mixed alkyl carboxylate complex related to alkylaluminium activation in diene polymerization catalysis

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$[(C_5Me_5)_2Sm(\mu\text{-}O_2CPh)]_2$ reacts with $^iBu_3Al$ to form a mixed bridge samarium aluminium complex $[(C_5Me_5)_2Sm(\mu\text{-}O_2CPh)(\mu\text{-}^iBu)Al(^iBu)_2]$, that displays two different carboxylate orientations toward the metals in a single crystal.

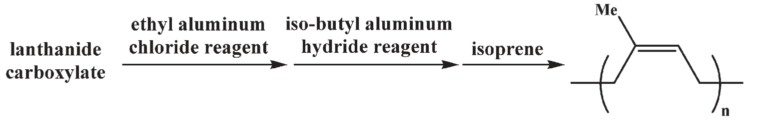
Organoaluminium complexes are frequently used to activate early transition metal and lanthanide compounds for catalysis, particularly for olefin polymerization.[1] Typically, the organoaluminium species are used to abstract ligands from the coordination sphere of the other metal to provide active sites.[2] Inherent in this process is a competition between the Lewis acidity of aluminium and the other electropositive metal. In general, it is assumed that if the organoaluminium compound is an effective activator, it has sufficient Lewis acidity to win the competition although large excesses of the aluminium reagent are often required. Detailed information on the intermediates in these abstraction processes is rarely available, however, to evaluate the abstraction reaction.

In the lanthanide-based polymerization of isoprene to high *cis*-1,4-polyisoprene, ethylaluminium chlorides and iso-butyl aluminium compounds are typically used sequentially to activate lanthanide carboxylates as shown in eqn (1).[3] The first step was initially thought to generate lanthanide trihalides that were subsequently alkylatedin the second step to make the "active catalyst" that contained at least one chloride and one alkyl functionality.[3,4] Subsequent studies with fully characterized lanthanide carboxylates have shown that ethylaluminium chloride reactions form products that retain aluminium.[5] Consistent with this, metallocene models of this lanthanide carboxylate–alkyl aluminium halide chemistry have shown that fully characterized bridged lanthanide aluminium complexes can form in these reactions, eqn (2).[6] Efforts to isolate intermediate mixed metal carboxylate complexes that presumably form before the final $(C_5Me_5)_2Sm(\mu\text{-}Cl)_2AlR_2$ products have been unsuccessful using a variety of R_2AlCl and R_3Al reagents until now.[7]

We report here that using $^iBu_3Al$ as a model alkylaluminium, a mixed metal carboxylate complex can be isolated that provides information on the relative Lewis acidity of aluminium *versus* samarium as these metals compete for the oxygen donor atoms. This study shows how delicately balanced the Lewis acidities may be. The unexpected stability of this intermediate with respect to loss of carboxylate from the lanthanide also raises interesting questions regarding the isoprene catalysis systems that use lanthanide carboxylates directly with only iso-butyl aluminium, catalysts that form mixtures of *cis*- and *trans*-polyisoprene.[8,9]

Yellow $[(C_5Me_5)_2Sm(\mu\text{-}O_2CPh)]_2$, **1**,[10] reacts with 2 equiv. of $^iBu_3Al$ in toluene to form an orange solution from which crystals can be isolated in 64% yield. X-ray crystallography revealed that the product, $(C_5Me_5)_2Sm(\mu\text{-}O_2CPh)(\mu\text{-}^iBu)Al(^iBu)_2$, **2**,† crystallized as a 1 : 1 mixture of two isomers in which the carboxylate bridging differed. The structures of the two components, **2a** and **2b**, are shown in Fig. 1 and eqn (3).

Complex **2** is the initial adduct expected from dissociation of dimeric **1** and complexation with Al^iBu_3. The ^1H NMR spectrum of the crude reaction mixture showed a set of resonances consistent with the $(C_5Me_5)_2Sm(O_2CPh)(^iBu)Al(^iBu)_2$ formula as well as resonances for the starting material, **1**, and a subsequent reaction product, $(C_5Me_5)_2Sm(\mu\text{-}^iBu)_2Al(^iBu)_2$, **3**.[11] Complex **3** is the end product analogous to that observed in eqn (2). The ^1H NMR spectrum of crystalline **2** in C_6D_6 invariably showed the presence of some **1** indicative of the equilibrium shown in eqn (3). Addition of more Al^iBu_3 to this mixture of complexes **1** and **2** does not



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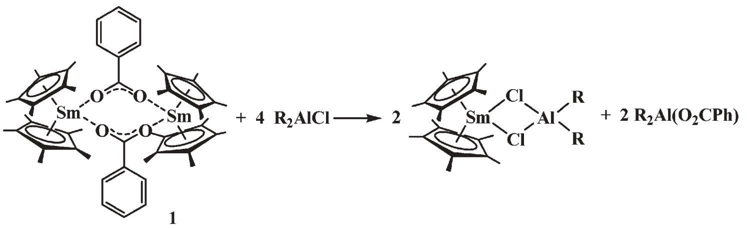

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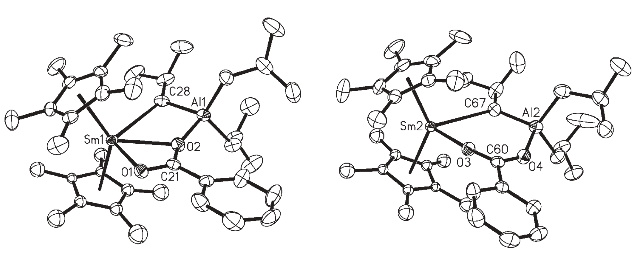

Fig. 1 Thermal ellipsoid plots for $(C_5Me_5)_2Sm(\mu\text{-}\eta^1{:}\eta^2\text{-}O_2CPh)(\mu\text{-}^iBu)Al(^iBu)_2$, **2a** (left), and $(C_5Me_5)_2Sm(\mu\text{-}\eta^1{:}\eta^1\text{-}O_2CPh)(\mu\text{-}^iBu)Al(^iBu)_2$, **2b** (right), with ellipsoids drawn at the 50% probability level (all hydrogen atoms have been omitted for clarity).

increase the concentration of **2**, but instead leads to **3** according to eqn (4). Consistent with eqn (3) and (4), a mixture of **1** and **3** does not form **2**.

This emphasizes the delicate balance that allows **2** to be isolated. Although there are several examples of adduct formation between lanthanide alkoxides and trialkyl aluminium,[12–14] to our knowledge there is only one other example of a structurally characterized adduct of a lanthanide carboxylate with trialkyl aluminium, $\{Me_2Al(O_2CC_6H_2{}^iPr_3\text{-}2,4,6)_2\}_2Nd(AlMe_4)$.[15]

Complex **2** not only is a model for the intermediate in alkylaluminium activation of a lanthanide carboxylate, but it also has an unusual structure that bears on the relative Lewis acidities of aluminium and samarium. In the crystal structure of **2**, the carboxylate does not have a single preference for bridging the samarium and aluminium metal centers in the solid state. In **2a**, the carboxylate attaches to samarium in a dihapto chelating mode and is monohapto to aluminium. In **2b**, the carboxylate is monohapto to both metals. The variable connectivity of the carboxylate ligand gives samarium formal coordination numbers of nine and eight in **2a** and **2b**, respectively. The isolation of two different coordination modes in a single crystal has been observed before in the structure of $\{Zr[\eta^1\text{-}OSi(O^tBu)_3]_4\}\{Zr[\eta^2\text{-}OSi(O^tBu)_3][\eta^1\text{-}OSi(O^tBu)_3]_3\}$.[16]

The structure of **2b** is the most conventional. The carboxylate bonding is delocalized with similar C–O bond distances (1.251(3) and 1.266(3) Å). The 2.277(2) Å O(3)–Sm(2) length is in the range of 2.202(4)–2.307(2) Å Sm–O(carboxylate) distances in the $[(C_5Me_5)_2Sm(\mu\text{-}\eta^1{:}\eta^1\text{-}O_2CR)]_2$ complexes (R = allyl, phenyl).[10] The 1.873(2) Å Al(2)–O(4) length is similar to reported Al–O carboxylate distances.[17–20] The 2.027(3) Å Al(2)–C(67) distance involving the bridging iso-butyl group is shorter than the 2.11(2) Å analog in **3** and the 2.962(3) Å C(67)–Sm(2) distance is much longer than the 2.74(1) Å analog in **3**. Hence, in **2b** the carboxylate appears to be positioned with normal M–O bond lengths between Sm and Al, but the bridging isobutyl group is more closely associated with Al than with Sm.

In **2a**, the bond distances around Al are similar to those in **2b**. Hence, the 1.900(2) Al(1)–O(2) distance is normal and the 2.020(3) Al(1)-C(28) length is short compared to the analog in **3**. In **2a**, the Sm-C(28) distance of 3.029(3) Å, Sm(1)–C(28), is even longer than that in **2b**. As a consequence, the bridging iso-butyl group is even more associated with Al than Sm. The carboxylate in **2a** is more localized with a 1.244(3) Å C(21)–O(1) distance *versus* a 1.301(3) Å C(21)–O(2) length. Both oxygen atoms are located much further from Sm than in **2b**: Sm(1)–O(2) is 2.543(2) Å and Sm(1)–O(1) is 2.421(2) Å. Interestingly, the carboxylate oxygen coordination puts the carboxylate carbon, C(21), within 2.883(3) Å of Sm(1), closer than the bridging isobutyl C(28).

The co-crystallization of **2a** and **2b** indicates that the carboxylate ligand can adopt more than one binding mode to samarium as the ligand bridges to aluminium. Both the almost trihapto arrangement with long distances in **2a** and the conventional monohapto coordination with a shorter distance in **2b** involve similar coordination to aluminium. In neither case, does the carboxylate show a definite preference for Al(III), although this metal is its ultimate partner after abstraction to form **3**. Since both **2a** and **2b** have the carboxylate ligand more closely attached to samarium than the bridging isobutyl group, these structures approximate intermediates in the substitution of iso-butyl for carboxylate on the samarium at an early stage in the transformation. Overall, this suggests that the relative Lewis acidities of the Sm and Al are closely balanced in this system. This may explain why five-fold excesses of reagent are commonly needed to drive eqn (2) and (4) to completion. This would also explain why a high ratio of Al : Ln is used in catalytic systems.

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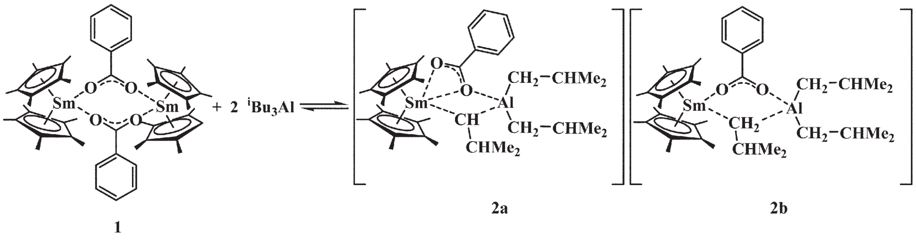

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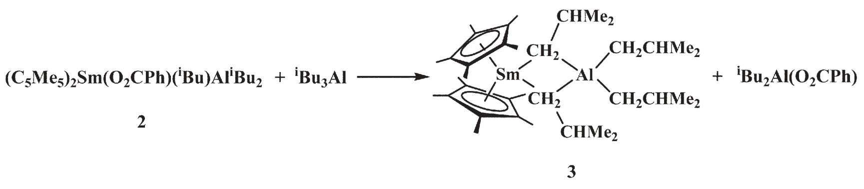

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Notes and references

† *Synthesis* of **2**: Under a nitrogen atmosphere with rigorous exclusion of air and water, a flask was charged with **1** (244 mg, 0.225 mmol) dissolved in 20 mL of toluene. ^{i}Bu$_3$Al (114 μL, 0.450 mmol) was added dropwise *via* syringe to the stirred solution. The reaction mixture changed from yellow to orange. After 12 h, toluene was removed leaving an orange oil which was subsequently extracted with hexane to form a concentrated solution. Orange crystals of **2** formed at −36 °C (72 mg, 43% yield). A second crop of crystals yielded additional material in 21% yield. Anal. Calcd. for C$_{39}$H$_{62}$O$_2$AlSm: C, 63.26; H, 8.46; Al, 3.65; Sm, 20.31. Found: C, 62.98; H, 8.47; Al, 3.52; Sm, 20.81%. ^{1}H NMR (C$_6$D$_6$) δ 0.85 (s, 30H, C$_5$*Me*$_5$), 7.8 (d, 2H, *o*-C$_6$*H*$_5$), 7.1 (t, 2H, *m*-C$_6$*H*$_5$), 3.4 (t, 1H, *p*-C$_6$*H*$_5$). Additional resonances were observed but could not be definitively assigned to individual iso-butyl protons in this paramagnetic system. ^{13}C NMR (C$_6$D$_6$) δ 134 (*o*-*C*$_6$H$_5$), 130 (*p*-*C*$_6$H$_5$), 124 (*m*-*C*$_6$H$_5$), 117 (*C*$_5$Me$_5$), 18.5 (C$_5$*Me*$_5$). *ipso* and carboxylate carbons were not located. IR (thin film, cm^{-1}) 2949 s, 2860 s, 2771 m, 2602 w, 1598 m, 1552 m, 1494 w, 1451 m, 1420 m, 1378 m, 1316 w, 1254 m, 1177 m, 1058 s, 1019 s, 842 s, 757 m, 714 m, 687 m. *Crystallographic data for* **2**: C$_{78}$H$_{124}$O$_4$Al$_2$Sm$_2$, M = 1480.43, triclinic, a = 14.0142(12), b = 16.4990(14), c = 17.2310(14) Å, α = 79.9810(10), β = 85.9860(10), γ = 85.1370(10)°, V = 3903.1(6) Å^3, T = 163(2) K, space group $P\bar{1}$, Z = 2, μ(Mo-Kα) = 1.556 mm^{-1}, 43498 reflections measured on a Siemens CCD diffractometer, 18880 unique (R_{int} = 0.0244) which were used in all calculations. The final $R1$ was 0.0303 ($I > 2.0\sigma(I)$) and w$R2$ (all data) was 0.0794. The SMART program package was used to determine the unit-cell parameters and for data collection (25 s per frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT and SADABS to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL program. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. Two of the pentamethylcyclopentadienyl ligands were disordered and included using multiple components with partial site-occupancy-factors. CCDC reference number 280597. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b511714c

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